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Electrical conductivity of degraded polyacrylonitrile powder by microwave irradiation for supercapacitor devices or other mobile applications

Spiridon Koutsonas

Ulster University/NIACE (North Ireland Advanced Composites Engineering Centre), Faculty Computing and Engineering/NIACE Advanced Composites and Engineering, Belfast, N.I., UK

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ABSTRACT

The primary aim of this article is to investigate and compare the static electric conductivity of degraded polyacrylonitrile powders under microwave irradiation in air. The resistivity of these materials was finally calculated. SEM analysis was used in order to characterize the most conductive powder. Polyacrylonitrile microwave conductivity may play an important role in the construction of high porosity area and so in electrochemical supercapacitor devices with high performances. Degradation of polyacrylonitrile carbon based nanoporous materials can be also used in the construction of fuel cells and in polymer lithium batteries.

1. Introduction to polymer conductivity

The field of conducting polymers has made significant growth during the past few years with a series of research articles. Conductivity is defined as the ability of a substance or organic compound to conduct electrical current. In a metal, the valence bands and conduction bands overlap and so negligible thermal energy is needed for an electron to move into a vacant state. In both insulators and semi-conductors there is an energy gap between the valence and conduction bands. In the absence of thermal energy, no electrons are excited to the conduction band and the materials are insulators [1–6]. Many types of conductive materials have been used with insulating carbon black (CB) polymers and metallic powders [1–6].

2. Description of the experimental set up

The materials used for this investigation were a series of polyacrylonitrile powder (provided by Sigma-Aldrich density 1184 Kg/m^3, refractive index n = 1.514, transition temperature T_m = 317 °C, average molecular weight M_w = 150,000) treated under microwaves thermally in air at different temperatures with a CEM Microwave apparatus.

For the instrumentation set up the following components were used: i) a power supply at 60 Watt max power, ii) a voltmeter, iii) a current meter, iv) a plunger at the end of which there was fixed a wire, v) cylindrical pieces of lead, vi) a measuring tape, vii) an insulating plastic tube was used as the length of comparison for the circle surface area used in the calculation of the conductivity, viii) a metallic base connected with two wires long about 0.1 m where the powder material was put on and ix) a square ceramic plate. Fig. 1a), show the components (i), (ii), (iii), (iv), (v) and (viii) connected in a circuit. Fig. 1b) show the layout of the instrumentation used.

With the aforementioned instrumentation the circuit of Fig. 1a) and b) above was set up the length L of the PAN powder inside the insulating plastic tube was measured each time. The diameter of the circular base of the insulating plastic tube was measured to be d = 0.01 m and so the radius r = 0.005 m.

All the investigation was based on the recorded measurements of current and voltage that were provided by the power supply to the PAN powder, which made part of the used circuit to be outlined in Section 4.

3. Theory of electrical measurements

The theory that facilitates the electrical conductivity measurements is the equations that are derived from Ohm's law:

$$V = I \cdot R \tag{1}$$

and the equation of the resistance:

$$R = \rho \cdot \frac{L}{A_{area}} \tag{2}$$

Combining the two we derived the equation of the resistivity ρ in terms of the measured voltage V and current I through the PAN powder

Email address: s.koutsonas@ulster.ac.uk (S. Koutsonas)

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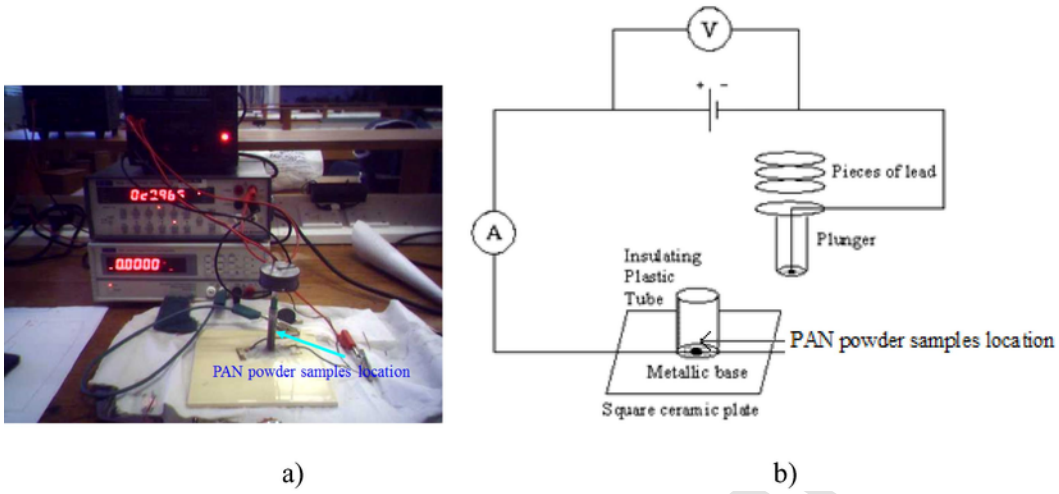

Fig. 1. a) Photo of the whole instrumentation that was used for the electrical conductivity measurements. b) Layout of the instrumentation design that was constructed for the conductivity measurements.

i.e.:

$$\rho = \frac{V \cdot A}{I \cdot L} \tag{3}$$

where is L the length of the powder inside an insulating plastic tube (see following section) and A is its circular base area.

The latter was calculated by the equation $A = \pi r^2$ with $r = 0.005\ m$ the radius of the insulating plastic tube. Finally with the aid of (3) and equation:

$$\sigma_{Sample} = \frac{1}{\rho} \tag{4}$$

the sample static electric conductivity σ can be calculated.

4. Conductivity measurements

In this section an account is provided of the conductivity measurements on PAN powder samples that had been previously treated in microwaves in air. The following table shows the minimum current measurements that were recorded as voltage was increased gradually. Brief comments follow for each sample letter.

(i) This PAN powder was treated by microwaves in CEM apparatus at 300 W, in air 101.325 kPa, and 90 °C for 1 hours of holding time. The voltage-current measurements yielded 58.202 V and 18×10^{-9} A respectively. The sample length $L = 0.0015$ m and Eqs. (3), (4) yield $\rho = 0.17 \times 10^{9}$ Ω·m and $\sigma = 5.88 \times 10^{-9}$ S/m.

(ii) This PAN powder was treated by microwaves in CEM at 300 W, 101.325 kPa, and 210 °C for 2.5 h of holding time. The measurements were 58.167 V for the voltage, 0.019 μA for the current and $L = 0.0015$ m for the sample length. Eqs. (3) and (4) yield $\rho = 0.16 \times 10^{9}$ Ω·m and $\sigma = 6.25 \times 10^{-9}$ S/m. Fig. 2 show the appearance of samples (i), (ii) after treatment.

(iii) This PAN powder sample was treated in air by microwaves with CEM at 300 W, 101.325 kPa, and 285 °C for 2.5 h holding time. The voltage was measured at 11.135 V and the current at 21.8 mA. The measured length was $L = 0.011$ m (change due at the different thickness of the carbon tested PAN material). Eqs. (3) and (4) yield $\rho = 364.7$ Ω·m and $\sigma = 2.74 \times 10^{-3}$ S/m.

(iv) For this PAN sample treated by microwaves in air CEM at 300 W, 101.325 kPa, at 300 °C after 4.5 h that it was observed the thermal runaway (TR). The measured voltage across this sample was 2.3 V and the current at 50.5 mA with a length $L = 0.01$ m. these values yield $\rho = 12.63$ Ω·m and $\sigma = 7.92 \times 10^{-2}$ S/m. This measurement shows that the exothermic reaction has helped increase the conductivity of PAN powder by 7 orders of magnitude compared to (i) results. Due to limitations with the instrumentation the TR, effect was not quantified precisely. This is due to vial glass

Fig. 2. a) Gold appearance of PAN polymer powder sample (i) treated in microwaves with CEM at 300 W, 0 psi, 90 °C for 1 h. b) Black appearance of PAN polymer powder sample (ii) treated in microwaves with CEM at 300 W, 101.325 kPa, 210 °C for 2.5 h.

melting and breaking because of the exothermic reaction it may be assumed that the temperature during the TR was in excess of 300 °C, around 800 °C which is the melting point of the vial glass. SEM analysis of the sample (iv) with the highest conductivity is presented on Fig. 3 with magnification at 10 μm and 4 μm.

5. Discussion

From the investigation the following points were observed:

a) The polyacrylonitrile powder is an insulator (conductivity < 10–10 S cm^{-1}) and remain an insulator under microwave treatment at (90–210) °C.
b) The microwave treatment can transform the PAN polymer powder from insulator to semiconductor (with 10–10 S cm^{-1} < conductivity < 10–3 S cm^{-1}) when treated at (285–300) °C and so to improve significantly the conductivity in our case until 7.92×10^{-2} S cm^{-1} after thermal runaway in excess of 300 °C.

It has proved difficult to pinpoint conductivity measurements on the same material and treatment as ours in the research literature. Therefore comparisons are based on similar but not identical work. For example, in reference by Yu Wang et.al [7], PAN/DMF (N-Dimethyl Formamide) precursor nano-fibres were pre-treated by pyrolysis between 77–1273 K for 0.5–2 h and have shown a rapid increase in conductivity (S/m) versus treatment temperature (K) and an even more rapid increase with pyrolysis time. These results could be viewed to lie partially in accordance to the increase shown by our fitting model for microwave treated PAN (point b) if this is extrapolated to higher temperatures.

Yu Wang et.al [7] investigated higher temperatures than our technical capabilities allowed and also longer treatment periods. However, there is an overlap in the treatment periods for up to 2.5 h and although the method of treatment was different in our study we can still attempt comparisons with the reported conductivities.

6. Conclusion

An experimental method for the quantitative evaluation and comparison of the conductivity of microwave treated PAN powder samples was reported. By measuring the voltages and currents across each microwave irradiated carbonised monolith PAN sample the values for the conductivity and resistivity were determined. After microwave treatment the carbonised PAN increased his conductivity by 7 orders magnitude so from insulator to semiconductor. SEM analysis of the final carbonised PAN product revealed the presence of macroporosity. This is a key element for the construction of degraded high surface area materials for use in supercapacitor devices or other mobile applications such as full cells and polymer batteries (see Table 1).

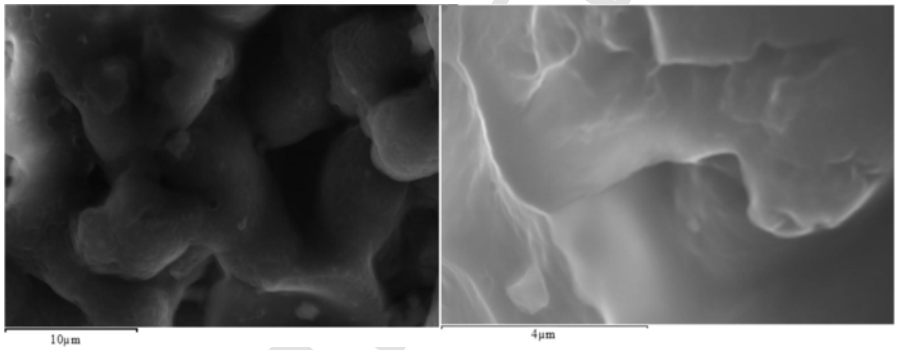

Fig. 3. SEM analysis at 20 kV of degraded PAN sample (iv) treated by microwaves in air CEM at 300 W, 101.325 kPa, at 300 °C after 4.5 h that it was observed the thermal runaway (TR).

Table 1
Conductivity measurements on 4 PAN microwave pre-treated samples, MT* = Microwave Temperature (during treatment), TT* = Treatment Time (microwaves).

PAN	Voltage	Current	Length	Resistivity	Conductivity	MT*	TT*
Sample	V (V)	I (A)	L (m)	ρ (Ω·m)	σ (S/m)	(°C)	(Hrs)
(i)	58.202	18×10^{-9}	0.0015	0.17×10^{9}	5.88×10^{-9}	90	1
(ii)	58.167	19×10^{-9}	0.0015	0.16×10^{9}	6.25×10^{-9}	210	2.5
(iii)	11.135	21.8×10^{-5}	0.011	364.7	2.74×10^{-3}	285	2.5
(iv)	2.3	1.43×10^{-3}	0.01	12.63	7.92×10^{-2}	> 300	4.5

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